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Applicant :	Richard E. Smalley et al	Art Unit :	1771
Serial No. :	09/722,950	Examiner :	Elizabeth M. Cole
Filed :	November 27, 2000	Conf. No. :	5035
Title :	ROPES OF SINGLE-WALL CARBON NANOTUBES AND COMPOSITIONS THEREOF		

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF KEN SMITH, Ph.D., UNDER 37 C.F.R. § 1.132

Dear Sir:

1. My name is Kenneth Smith, Ph.D.. I am the Vice President of Technology of Carbon Nanotechnologies, Inc., ("CNI"), which I co-founded with Dr. Richard Smalley, one of the named inventors of the above-reference patent application (the "Application"). CNI has exclusively licensed the Application from Rice University. In addition, I worked at Rice University with Dr. Richard Smalley and the other inventors of the Application when they invented the invention of the Application.

2. Attached hereto at Exhibit 1 is a true and correct copy of M.S. Dresselhaus, "Carbon-Based Nanostructures" (January 1998), pages 1-4, which was printed from the Internet on or about December 13, 2006.

3. Attached hereto at Exhibit 2 is a true and correct copy of excerpts from The World Technology Evaluation Center Report on "R&D Status and Trends in Nanoparticles, Nanostructures Materials, and Nanodevices in the United States," May 8-9, 1997 Workshop, cover pages and pages 169-171, which was printed from the Internet on or about December 13, 2006.

4. Attached hereto at Exhibit 3 is a true and correct of *The Wondrous World of Carbon Nanotubes, a review of current carbon nanotube technologies*, Eindhoven University of Technology, (27 February 2003), at pages 1, 14, & 23, which was printed from the Internet on or about December 13, 2006.

5. Attached hereto at Exhibit 4 is true and correct copy of N. Braidy, *et al.*, "Single-Wall Carbon Nanotubes Synthesis by Means of UV Laser Vaporization: Effects of the Furnace Temperature and the Laser Intensity Processing Parameters," *Mat. Res. Soc. Symp. Proc.*, Vol. 703, V9.31.1-6 (2002), which was printed from the Internet on or about December 13, 2006.

6. Attached hereto at Exhibit 5 is a true and correct copy of "Carbon Nanotubes," *physicsweb*, Institute of Physics Publishing (January 1998), which was printed from the Internet on or about December 13, 2006.

7. The above cited materials, which are attached hereto, are representative of many other materials similarly identifying and recognizing the invention of the present Application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: December 15, 2006

By



Ken Smith, Ph.D.

EXHIBIT 1

CARBON-BASED NANOSTRUCTURES

M.S. Dresselhaus

Department of Electrical Engineering and Computer Science and Department of Physics
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Cambridge, MA 02139

Materials Categories

The carbon-based nanostructural materials considered here include fullerenes and related materials, carbon nanotubes, carbon nanoparticles, and porous carbons, including activated carbon fibers and carbon aerogels.

Scientific Drivers

Carbon nanotubes (~1 nm in diameter) are presently the hottest carbon nanostructured material. Single-wall carbon nanotubes, consisting of a cylindrical tube one atomic layer in thickness, are predicted to be either semiconducting or metallic depending on the diameter and chirality of the nanotube. These unusual electronic properties imply novel 1D physics. In addition, single electron (Coulomb blockade) transport phenomena are now being studied in this unique system using nanolithographic techniques. The joining of two dissimilar nanotubes has been predicted to give rise to semiconductor-metal heterojunctions with properties that can be modified by perturbing the junction region, which is of ~1 nm size. Remarkable quantum effects are also predicted and observed for the phonons in carbon nanotubes, also dependent on the diameter and chirality of the nanotubes. Another area of great excitement concerns the elastic properties, especially the extremely high Young's modulus for carbon nanotubes. Applications of carbon nanotubes are under development for displays and for tips for scanning tunneling microscopes and for the manipulation of nanostructures. It is expected that the physical properties of the carbon nanotubes can be significantly modified by intercalation, as for example by using alkali metal dopants, but this is a very new research area, with only a few results now in press.

Fullerenes represent a unique category of cage molecules with a wide range of sizes, shapes, and molecular weights. Most of the effort thus far has gone into the study of C_{60} fullerenes, which can now be prepared to a purity of parts per thousand. Since every C_{60} molecule is like every other one, ignoring ^{12}C and ^{13}C isotope effects, C_{60} provides a unique monodisperse prototype nanostructure assembly with particle size of 0.7 nm. Because of the unique icosahedral symmetry of C_{60} , these molecules provide prototype systems for spectroscopy, optics, and other basic science investigations. Study of the structure and properties of the whole family of fullerene cage molecules, together with their endohedral cousins (formed by insertion of guest species, usually rare earth or transition metals, within the cage) is being pursued worldwide. A few groups are also coating fullerene molecules with one or more layers of alkali metals and alkaline earths and studying their remarkable structures and properties. The intercalation of alkali metals and other species into the crystalline C_{60} lattice alters the structure and leads to large modifications in properties. The special properties of the metallic and superconducting phases thus achieved are of fundamental significance. The new phases associated with polymerization of C_{60} by incident light, pressure, and alkali metal doping are of both scientific and practical interest.

Carbon nanoparticles can be all carbon (such as the so-called carbon onions), or carbon-coated particles

consisting of carbon layers wrapped around other materials, usually carbides. Studies of carbon onions have emphasized the basic science of nanostructure growth in carbon systems, while the carbon-coated nanoparticles have combined both basic studies, concerning their growth and structure, with applications, particularly for magnetic nanoparticles. The carbon coating provides a means for stabilizing and separating small particles containing active ingredients with special properties that may, for example, be useful for magnetic information storage.

Porous carbons, such as activated carbon fibers and carbon aerogels, have a high density of pores, with pore sizes < 2 nm. The structure and properties of these nanopores have been investigated both for their scientific interest and for practical applications, utilizing the special properties of high surface area materials. Remarkably high specific surface areas, as high as ~ 3000 m²/g, are achievable in these materials.

Critical Control Parameters

The critical control parameters of individual carbon nanotubes are the nanotube diameter and chirality, while the packing density is important for nanotube arrays. Most of the presently used single-wall carbon nanotubes have been synthesized by a pulsed laser vaporization method, pioneered by the Smalley group at Rice University. Their synthesis result of 1996 represents a major breakthrough in the field. There are several oral reports that a catalyzed carbon arc synthesis route also can be used to produce high yields of nanotubes with a diameter distribution similar to those obtained by the Rice group. There are presently many groups worldwide working to develop more efficient synthesis techniques for producing arrays of similar single-wall nanotubes, with a narrow diameter and chirality distribution, at a high production rate, and at a cheap cost. Right now, it is possible through Smalley's recent work to produce significant amounts of (10,10) armchair nanotubes with a small average diameter (~ 1.3 nm) and a small diameter distribution. Much effort is presently being expended to develop production methods to provide control in the synthesis of armchair nanotubes arrays with different diameters, let alone the controlled synthesis of nanotube arrays with different chiralities. This field is very new, and many groups are now trying to reproduce the sample quality achieved by the Rice group. There is optimism in the community that much progress will be made within the coming year toward improving synthesis capability and properties control for the single-wall nanotubes, by study of the growth conditions, such as temperature, pressure, and kinetics. Computer simulations are being actively employed to improve convergence of the experimental approaches. Considerable effort is also being expended in the study of intercalation as a method for modifying the properties of the nanotubes. Efforts to improve the synthesis of multiwall nanotubes (containing several coaxial single wall nanotubes) continues, with diameters up to ~ 15 nm defining the nanotube range, and with diameters in the range $15 < d < 100$ nm defining the nanofiber range where faceting of the individual "tubes" occurs at high heat treatment temperature (> 2500 °C).

The important parameters describing fullerene cage molecules include the number n of carbon atoms in the particular fullerene species C_n , and the shape of each of the isomers corresponding to C_n . In the case of the endohedral fullerenes, the number of guest atoms as well as the guest species needs to be controlled, in addition to the mass and isomer type of the fullerene host. In general, the whole gamut of fullerene masses and isomers are formed simultaneously. While some control of the arc discharge conditions (or of other synthesis methods such as laser vaporization or flame methods) can be used to modify the mass and isomer distribution of the synthesis process, most effort has been expended on efficient and sensitive separation methods. These methods are easiest to implement for the lighter fullerenes. Separation according to molecular weight is first accomplished by advanced chromatography methods. Purification of each of the isomers at a given mass value is more difficult, and only limited success has been achieved thus far. Efforts to improve the efficiency of the synthesis process and the

purity of C_{60} as a reagent are now largely being carried out in the commercial arena. To a large degree this is also true of C_{70} . Basic research is now being directed toward gaining a fundamental understanding of the growth mechanism and fundamentally new synthesis routes, based, for example, on the building block carbon clusters found in C_{60} . There are also serious efforts by many research groups worldwide to produce larger quantities of higher purity higher fullerenes -- C_{70} , C_{76} , C_{84} , etc. -- using advanced chromatography, along with other specialized techniques. Many of the same groups are also active in synthesizing, separating, and purifying endohedral fullerenes.

Carbon-coated nanoparticles, produced by arc discharge methods or by laser vaporization techniques, are characterized by their size and shape distribution, the thickness of the carbon coating relative to the particle diameter, and the stoichiometry, crystallinity, and homogeneity of the phase of the enclosed carbide or other constituent. Conditions of temperature, cooling rates, gas transport agents, and other process conditions affect the physical parameters and therefore properties of the nanoparticles. In the case of carbon-coated nanoparticles, basic research on process control, structure, and properties is actively being carried out, mostly in universities, with some start-up companies working on the improvement of the synthesis process, on scale-up, and on controlling costs. The parameters characterizing the nanostructure aspects of porous carbons focus on pore size and pore size distribution. Among the various activated carbons, all of which have a large concentration of nanopores, it is the activated carbon fibers that have the smallest pore size distribution. The pore size and its distribution are sensitive to the temperature and pressure of the steam and CO_2 used in the activation process. Carbon aerogels have a much wider range of size distributions, with nanopores found within the small particles in the carbon aerogel chains, and with mesopores and macropores found between the particles and between clusters of particles. The average nanopore size and the nanopore size distribution depend on the precursor materials used in the aerogel synthesis, the carbonization temperature and time, and other process parameters. Steady progress has been made in varying the process conditions to control and vary the diameter distributions of the pores. Activation of carbon aerogels has been demonstrated as a method for adding a high density of nanopores, but this is a new research area that has not yet been widely studied.

Commercialization Considerations

Whereas the quantum aspects of single-wall carbon nanotubes are at an early stage of research, the more general desirable properties of carbon nanotubes are already being exploited commercially. Multiwall carbon nanofibers are presently being used as conductive additives to plastics and in electrochemical capacitor applications. Such commercial applications of nanofibers do not impose severe requirements on uniformity in nanotube diameter and sample homogeneity from one nanotube to another. Carbon fibers in the 1-10 micron range have been produced commercially for several decades. Incremental improvements in the manufacturing process have continued over this time period, leading to enhanced product performance and reliability; however, the relatively high price of the product has restricted the available markets. The same constraints may also apply to the commercialization of carbon nanotubes exhibiting the remarkable and unique 1D properties described above.

Synthesis of C_{60} and C_{70} is now a commercial process, with continuing increases in purity and decreases in cost. As more fullerene applications become commercialized, the demand for C_{60} and C_{70} will increase, and further improvements in the products and reductions in cost are expected. The commercialization of higher fullerenes and endohedral fullerenes is hampered by present limitations on efficient synthesis, separation and purification techniques, and the absence of significant products based on these materials.

Carbon-coated nanoparticles have moved quite rapidly into the commercial sector. Several start-up companies are developing niche proprietary applications and are working on issues of scale-up, reproducibility, reliability, and cost, while basic and applied R&D continue actively in university and industrial laboratories.

Porous carbons have been commercialized for a relatively long period of time for gas adsorption, environmental cleanup, heavy metal and ion separations, and electrical capacitor applications. As control of the pore size distribution has increased and cost has been reduced, these materials have found more applications and markets. Both large companies and start-up companies are involved with these products.

In all carbon nanostructured materials, cost has been a main factor in limiting commercialization, yet it is widely believed that if production volumes increase, costs would decrease markedly, thereby significantly increasing the utilization of the excellent properties of nanostructured carbon.



Published: January 1998: WTEC Hyper-Librarian

EXHIBIT 2



World Technology Evaluation Center (WTEC)



NIST

WTEC Workshop Report on

R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States

Proceedings of the May 8-9, 1997 Workshop

Richard W. Siegel, WTEC Panel Chair
Evelyn Hu, Panel Co-Chair
M.C. Roco, NSF Coordinator

JANUARY 1998



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WTEC PANEL ON NANOPARTICLES, NANOSTRUCTURED MATERIALS, AND NANODEVICES

Sponsored by the National Science Foundation, the Air Force Office of Scientific Research, the Office of Naval Research, the Department of Commerce (including NIST and Technology Administration, Main Commerce), the Department of Energy, the National Institutes of Health, and the National Aeronautics and Space Administration of the United States Government.

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INTERNATIONAL TECHNOLOGY RESEARCH INSTITUTE WTEC PROGRAM

The World Technology Evaluation Center (WTEC) at Loyola College (previously known as the Japanese Technology Evaluation Center, JTEC) provides assessments of foreign research and development in selected technologies under a cooperative agreement with the National Science Foundation (NSF). Loyola's International Technology Research Institute (ITRI), R.D. Shelton, Director, is the umbrella organization for WTEC. Paul Heret, Senior Advisor for Planning and Technology Evaluation at NSF's Engineering Directorate, is NSF Program Director for WTEC. Several other U.S. government agencies provide support for the program through NSF.

WTEC's mission is to inform U.S. policymakers, strategic planners, and managers of the state of selected technologies in foreign countries in comparison to the United States. WTEC assessments cover basic research, advanced development, and applications. Panels of typically six technical experts conduct WTEC assessments. Panelists are leading authorities in their field, technically active, and knowledgeable about U.S. and foreign research programs. As part of the assessment process, panels visit and carry out extensive discussions with foreign scientists and engineers in their labs.

The ITRI staff at Loyola College help select topics, recruit expert panelists, arrange study visits to foreign laboratories, organize workshop presentations, and finally, edit and disseminate the final reports.

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WTEC Study on

NANOPARTICLES, NANOSTRUCTURED MATERIALS, AND NANODEVICES

PART I: PROCEEDINGS OF THE MAY 8-9, 1997 U.S. REVIEW WORKSHOP

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Carbon-coated nanoparticles, produced by arc discharge methods or by laser vaporization techniques, are characterized by their size and shape distribution, the thickness of the carbon coating relative to the particle diameter, and the stoichiometry, crystallinity, and homogeneity of the phase of the enclashed carbide or other constituent. Conditions of temperature, cooling rates, gas transport agents, and other process conditions affect the physical parameters and therefore properties of the nanoparticles. In the case of carbon-coated nanoparticles, basic research on process control, structure, and properties is actively being carried out, mostly

in universities, with some start-up companies working on the improvement of the synthesis process, on scale-up, and on controlling costs.

The parameters characterizing the nanostructure aspects of porous carbons focus on pore size and pore size distribution. Among the various activated carbons, all of which have a large concentration of nanopores, it is the activated carbon fibers that have the smallest pore size distribution. The pore size and its distribution are sensitive to the temperature and pressure of the steam and CO_2 used in the activation process. Carbon aerogels have a much wider range of size distributions, with nanopores found within the small particles in the carbon aerogel chains, and with mesopores and macropores found between the particles and between clusters of particles. The average nanopore size and the nanopore size distribution depend on the precursor materials used in the aerogel synthesis, the carbonization temperature and time, and other process parameters. Steady progress has been made in varying the process conditions to control and vary the diameter distributions of the pores. Activation of carbon aerogels has been demonstrated as a method for adding a high density of nanopores, but this is a new research area that has not yet been widely studied.

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In all carbon nanostructured materials, cost has been a main factor in limiting commercialization, yet it is widely believed that if production volumes increase, costs would decrease markedly, thereby significantly increasing the utilization of the excellent properties of nanostructured carbon.

EXHIBIT 3

The Wondrous World of Carbon Nanotubes

'a review of current carbon nanotube technologies'



27 February 2003

The multidisciplinair project group consists of the following people:

M. Duenen (N)
R.D. de Fouw (ST)
B. Hamers (ST, Treasurer)
P.G.A. Janssen (ST)
K. Schouteden (N)
M.A.J. Veld (ST, Project Manager)

Tutor:	X.E.E. Reynhout (TU/e)
Coordinator:	Dr. Ir. J.C. Reijnga (TU/e)
Client:	Prof. dr. P.H.L. Notten (Philips)
Advisor:	Ir. R.A.H. Niessen (Philips)

2.4 Laser ablation

In 1995, Smalley's group²³ at Rice University reported the synthesis of carbon nanotubes by laser vaporisation. The laser vaporisation apparatus used by Smalley's group is shown in Figure 2-9. A pulsed^{26,27}, or continuous^{28,29} laser is used to vaporise a graphite target in an oven at 1200 °C. The main difference between continuous and pulsed laser, is that the pulsed laser demands a much higher light intensity (100 kW/cm² compared with 12 kW/cm²). The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. As the vaporised species cool, small carbon molecules and atoms quickly condense to form larger clusters, possibly including fullerenes. The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures.³⁰ Catalysts may even open cage structures when they attach to them. From these initial clusters, tubular molecules grow into single-wall carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der Waals forces³⁰.

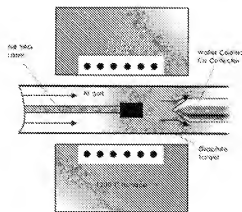


Figure 2-9: Schematic drawings of a laser ablation apparatus.

There are some striking, but not exact similarities, in the comparison of the spectral emission of excited species in laser ablation of a composite graphite target with that of laser-irradiated C₆₀ vapour. This suggests that fullerenes are also produced by laser ablation of catalyst-filled graphite, as is the case when no catalysts are included in the target. However, subsequent laser pulses excite fullerenes to emit C₂ that adsorbs on catalyst particles and feeds SWNT growth. However, there is insufficient evidence to conclude this with certainty³⁰.

Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism.

2.4.1 SWNT versus MWNT

The condensates obtained by laser ablation are contaminated with carbon nanotubes and carbon nanoparticles. In the case of pure graphite electrodes, MWNTs would be synthesised, but uniform SWNTs could be synthesised if a mixture of graphite with Co, Ni, Fe or Y was used instead of pure graphite. SWNTs synthesised this way exist as 'ropes', see Figure 2-10^{30,30}. Laser vaporisation results in a higher yield for SWNT synthesis and the nanotubes have better properties and a narrower size distribution than SWNTs produced by arc-discharge.

Nanotubes produced by laser ablation are purer (up to about 90 % purity) than those produced in the arc discharge process. The Ni/Y mixture catalyst (Ni/Y is 4.2/1) gave the best yield.

Summary

In Table 2-2, a short summary of the three most common techniques used nowadays is given.

	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Method			
Who	Ebbesen and Ajayan, NEC, Japan 1992 ¹⁵	Endo, Shinshu University, Nagano, Japan ²³	Smalley, Rice, 1995 ¹⁶
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

Table 2-2: A summary of the major production methods and their efficiency

EXHIBIT 4

Single-Wall Carbon Nanotubes Synthesis by Means of UV Laser Vaporization: Effects of the Furnace Temperature and the Laser Intensity Processing Parameters

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ABSTRACT

Carbon single-wall nanotubes (SWNTs) have been successfully synthesized by means of KrF laser vaporization of a Co-Ni-doped graphite pellet in a flowing argon atmosphere. The effects of two key processing parameters, namely the furnace temperature (in the 25-1150 °C range) and the laser intensity (in the $0.8-4.4 \times 10^8$ W/cm² range), on the yield and the structural characteristics of the carbon SWNTs were investigated. By characterizing the obtained deposits by means of transmission electron microscopy and micro-Raman spectroscopy techniques, we were able to identify a threshold temperature as low as ~550 °C, below which no carbon SWNTs can be grown. The increase of the furnace temperature from 550 to 1150 °C was found to lead not only to a significant increase in the SWNTs yield but also to the formation of larger SWNTs bundles. Raman analysis have also revealed that the diameter distribution peak shifts from ~1.05 to ~1.22 nm as the temperature is raised from 550 to 1150 °C. At the highest furnace temperature of 1150 °C, we also found that a minimum laser intensity of about 1.6×10^8 W/cm² is required to grow carbon SWNTs by means of the KrF laser. Higher laser intensities have resulted in a higher yield of SWNTs with relatively thicker bundles. Moreover, the increase of the laser intensity was found to promote the growth of 1.22 nm-diameter nanotubes to the detriment of thinner carbon nanotubes (1.05 and 1.13 nm-diameters).

INTRODUCTION

Since the first demonstration in 1995 of the use of a Q-switch Nd:YAG laser as a new alternative to synthesize single-wall carbon nanotubes [1], the field of laser synthesis of carbon nanotubes continues to attract great interest for either fundamental or applications purposes. Indeed, the laser vaporization technique stands out by its capacity to produce exclusively single-wall nanotubes (SWNTs) at the highest yield ever reported (~80 %) [2]. Focus has been put on the study of the effect of many processing parameters in order to optimize the technique. For example, the influence of the furnace temperature was investigated for dual pulse Nd:YAG laser [3] and pulsed CO₂ laser [4] to conclude that a higher furnace temperature leads not only to the production of a higher fraction of SWNTs (against other carbonaceous species) but also to a preferential growth of SWNTs of larger diameters. Other studies have reported on the influence of laser intensity for single and/or dual pulse Nd:YAG laser and established the existence of an optimal laser intensity at which SWNTs are preferentially grown [5, 6]. On the other hand, all the research reported to date on the laser synthesis of SWNTs was carried out using lasers emitting in the visible and/or infrared (from 532 nm to 10.6 µm) part of the spectrum. The growth of carbon nanotubes by using lasers emitting in the UV domain remains unexplored.

In this paper, we report on the successful synthesis of SWNTs by means of UV laser vaporization. We will focus here on the study of the influence of two processing parameters, namely the furnace temperature and the laser intensity, on the growth of SWNTs. In particular, it is found that carbon SWNTs can be grown by means of KrF laser vaporization at a temperature (550 °C) lower than the lowest temperature (850 °C) required when using Nd:YAG lasers.

EXPERIMENTAL

Carbon SWNTs were produced by ablating a Co-Ni-doped graphite pellet by means of a pulsed KrF excimer laser (wavelength = 248 nm; pulse duration = 15 ns; repetition rate = 30 Hz). The target was fabricated by pressing a mixture of a graphite powder (-325 mesh), a carbon cement and Co-Ni powder catalyst (0.6% at.) at a pressure of 5 kPsi. The obtained pellet is cured at 800°C for 8h, heated at 1150 °C for 12h in a flowing argon atmosphere and then placed in a quartz tube in the center of the furnace. During synthesis, the laser beam was rastered over the target surface in order to ensure a uniform ablation. KrF laser vaporization was carried out in a flowing argon atmosphere (300 SCCM, 500 Torr) at different furnace temperatures ranging from room temperature (RT) to 1150 °C and with various on-target laser intensities in the $(0.8-4.4) \times 10^8$ W/cm² range. The laser vaporized species were carried by the flowing argon gas towards a water-cooled copper collector, located at the exit end of the furnace, on which the nanotubes were collected.

The as-produced carbon deposits (no purification processing was used) were systematically characterized as a function of the processing parameters by means of : (i) transmission electron microscopy (TEM) (FEG Philips CM20 microscope, acceleration voltage of 200kV), (ii) high-resolution TEM (HRTEM) imaging (Gatan image filter multiscan camera) and (iii) micro-Raman spectroscopy (Renishaw Imaging Microscope Wire^{PM}, argon ion excitation with $\lambda_{exc} = 514.5$ nm).

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the samples produced at various furnace temperatures ranging from RT to 1150°C with a KrF laser intensity of 3.5×10^8 W/cm². The Raman peaks in the low frequency region (100-300 cm⁻¹) are due to the radial breathing modes (RBM) of the nanotubes, and their position (ω in cm⁻¹) can be directly related to the nanotube diameter (d in nm) by using the relation ($d = 223.75/\omega$) proposed by Bandow *et al.* [3]. For furnace temperatures < 550 °C, the absence of RBM peaks in the low-frequency part of the Raman spectra clearly indicates that no nanotubes were formed at these low temperatures. In contrast, the strong scattering RBM peaks observed for temperatures ≥ 550 °C are a typical signature of SWNT containing samples. Indeed, the main peaks (centered around 183, 198 and 213 cm⁻¹) that compose the RBM band are due to carbon SWNTs having diameters of 1.22, 1.13 and 1.05 nm, respectively. As the furnace temperature is raised from 550 to 1150 °C, the RBM peak assigned to the 1.22 nm nanotubes becomes more intense to the detriment of the 1.05 and 1.13 nm-diameter nanotubes. This shift of the maximum of the nanotube diameter distribution (from 1.05 to 1.22 nm) suggests that the furnace temperature increase favors the growth of thicker nanotubes. The increase of the nanotube diameter with the growth temperature has been also observed for SWNTs produced by means of dual pulse Nd:YAG laser configuration [3].

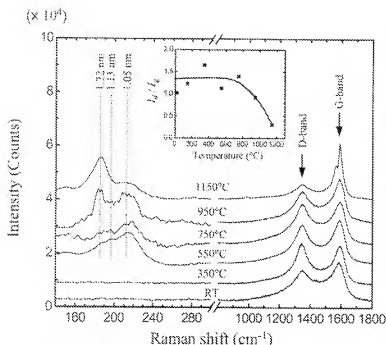


Figure 1. Raman spectra of the UV laser produced deposits at various furnace temperatures ranging from RT to 1150 °C. The RBM Raman peaks are identified (dashed vertical lines) along with their corresponding carbon SWNT diameters in nm. The inset shows the variation of the I_D/I_G ratio of the deposits as a function of the furnace temperature.

The high-frequency G and D Raman bands are due to the graphitic E_{2g} tangential acoustic mode of the SWNTs and to disordered sp^2 carbon, respectively [7]. The ratio of the intensities of the D-band to the G-band (I_D/I_G) is proportional to the relative amount of amorphous carbon or other disordered sp^2 carbon species [7]. The inset of figure 1 shows that the I_D/I_G ratio oscillates around an average value of $\sim 1.3 \pm 0.3$ for furnace temperatures ≤ 750 °C, and then steadily decreases for higher temperatures to reach a value of ~ 0.3 at 1150 °C. This indicates that high processing temperatures lead to a lower fraction of disordered carbon in the deposits. The resonant enhancement of the G-band (which is a consequence of the high yield of SWNTs observed at high temperatures) may also contribute to the observed lowering of the I_D/I_G ratio.

Figure 2 shows the typical TEM micrographs of the deposits at selected furnace temperatures. At a furnace temperature of 350 °C, an extensive search failed to uncover any SWNT in the deposit (this is consistent with the absence of the RBM band in the corresponding Raman spectrum). The carbon soot was rather composed of graphitic cages having a concentric layer morphology and an average diameter in the 5-10 nm range (inset of Fig. 2a). At a temperature of 550 °C, bundles of SWNTs having diameters ranging from 10 to 15 nm were found in low yield. Figure 2b is a typical TEM image of the deposits synthesized at 550 °C where a loop-like bundle having 14 nm in diameter and ~ 1.4 μ m in length is clearly observed (The HRTEM micrograph shown in the inset of Fig. 2b confirms the typical internal structure of a SWNT bundle). In addition to the nanotubes, the carbon nanostructures that compose also the deposit at 550°C were found to consist of interconnected fullerene-like structures [8]. When the furnace temperature is raised to 1150°C, the deposit was found to contain a significantly higher fraction of SWNTs (Fig. 2c) self-organized in larger bundles (15-20 nm-diameter). Moreover, the average diameter of the SWNTs was found to be 1.2 ± 0.3 nm, as deduced from HRTEM micrographs using direct lattice images of nanotubes bundles lying parallel to the microscope focal plane [2]. At 1150°C, the carbon nanoparticles co-produced with the SWNTs were found

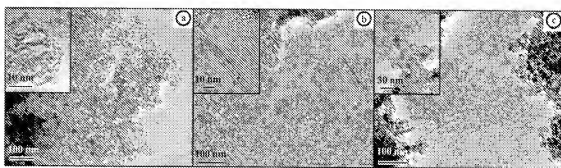


Figure 2. TEM micrographs of the deposits grown at (a) 350 °C, (b) 550 °C and (c) 1150 °C furnace temperatures.

to have a diameter in the 30-50 nm range and were most often constituted of amorphous carbon surrounding catalyst nanoclusters (see inset of Fig. 2c).

At the highest furnace temperature of 1150 °C, the effect of the laser intensity on the growth of SWNTs was investigated over the $0.8\text{--}4.4 \times 10^8 \text{ W/cm}^2$ range. A laser intensity of $1.6 \times 10^8 \text{ W/cm}^2$ was identified as the lowest value that produces sufficient amount of SWNTs containing soot that permits subsequent characterizations. Figure 3 displays the Raman spectra of the SWNT samples produced at increasing laser intensities. The RBM band clearly indicates the presence of carbon nanotubes having diameters in the (1.05- 1.50) nm range. One can note that as the laser intensity is increased, the 1.22 nm-diameter peak becomes sharper and more intense to the detriment of the other components. A tendency to favor the formation of nanotubes with larger diameters as the laser intensity is increased have been also reported when Nd:YAG lasers were used [6,9].

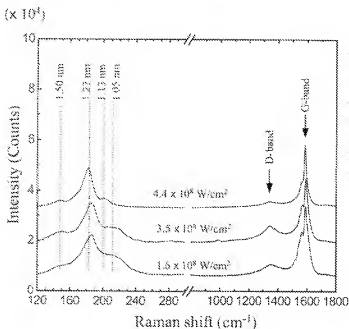


Figure 3. Raman spectra of the SWNTs synthesized by means of UV laser vaporization at 1150 °C with various laser intensities. The RBM Raman peaks are identified (dashed vertical lines) along with their corresponding carbon SWNT diameters in nm.

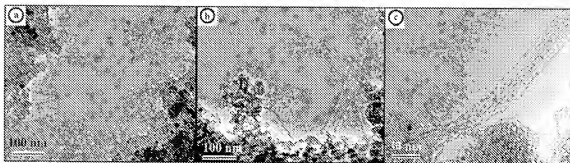


Figure 4. TEM micrographs of SWNT samples produced at 1150 °C with various KrF laser intensities: (a) 2.7×10^8 W/cm², (b) 3.5×10^8 W/cm² and (c) 4.4×10^8 W/cm².

Figure 4 shows TEM micrographs taken from SWNT samples produced at different laser intensities. At low laser intensities (1.6 – 2.7×10^8 W/cm²), the deposit is constituted of SWNT bundles having an average diameter of 12 nm along with catalyst nanoclusters embedded within a carbon nanoparticles (30–50 nm-diameter). The morphology and the diameter of these particles were found to remain insensitive to the laser intensity over all the investigated range. However, the fraction of nanotubes in the deposits was found to increase as the laser intensity is raised to 3.5 and 4.4×10^8 W/cm². The diameter of the SWNT bundles also increases with the laser intensity. SWNT bundles having a diameter of up to ~30 nm were observed at the highest laser intensity investigated here (see Fig. 4c).

CONCLUSION

The synthesis of single-wall carbon nanotubes by means of KrF laser vaporization is demonstrated. It is shown that SWNTs can be grown at a temperature as low as 550 °C. At a furnace temperature of 1150 °C, it is found that a minimum laser intensity of about 1.6×10^8 W/cm² is required to produce carbon SWNTs. The obtained results show that the increase of the furnace temperature leads to a higher yield of SWNTs and favors the growth of larger SWNTs organized in thicker bundles. Similar effects, but at a lesser degree, were also observed with the increase of the laser intensity. Such a similarity could be explained by considering that an increase of the laser intensity would lead to an enhancement of the temperature of the surface target during laser vaporization. Indeed, for the relatively low laser intensities investigated here, a major part of the laser energy is expected to be absorbed at the target near-surface, acting thereby as a local furnace. Finally, the extension of the useful laser wavelengths to the UV domain not only offers a new alternative to produce efficiently SWNTs, but might also open new prospects in the fundamental and/or application aspects of laser synthesized nanotubes.

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EXHIBIT 5

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Carbon nanotubes

Feature: January 1998

Theory suggests that carbon nanotubes have a variety of useful properties, and experiments to test these predictions are just becoming possible.

Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. Interest from the research community first focused on their exotic electronic properties, since nanotubes can be considered as prototypes for a one-dimensional quantum wire. As other useful properties have been discovered, particularly strength, interest has grown in potential applications. Carbon nanotubes could be used, for example, in nanometre-sized electronics or to strengthen polymer materials.

An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. Just a nanometre across, the cylinder can be tens of microns long, and each end is "capped" with half of a fullerene molecule. Single-wall nanotubes can be thought of as the fundamental cylindrical structure, and these form the building blocks of both multi-wall nanotubes and the ordered arrays of single-wall nanotubes called ropes. Many theoretical studies have predicted the properties of single-wall nanotubes.

It appears that the first carbon filaments of nanometre dimensions were prepared in the 1970s by Morinobu Endo, as part of his PhD studies at the University of Orleans in France. He grew carbon fibres about 7 nm in diameter using a vapour-growth technique, but these filaments were not recognized as nanotubes and were not studied systematically. It was not until 1991, when Sumio Iijima of the NEC Laboratory in Tsukuba used high-resolution transmission electron microscopy to observe carbon nanotubes, that the field really started to take off. Researchers at the Institute of Chemical Physics in Moscow independently discovered carbon nanotubes and nanotube bundles at about the same time, but these generally had a much smaller length-to-diameter ratio. The shape of these nanotubes led the Russian researchers to call them "barrelenes".

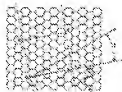


figure 1

The discovery of fullerenes by Harold Kroto of Sussex University in the UK and Richard Smalley and co-workers at Rice University in the US stimulated researchers to explore carbon filaments further. Indeed, the realization that the ends of carbon nanotubes must be fullerene-like "caps" explained the fact that the diameter of a carbon nanotube could only be as small as a fullerene molecule.

Although Iijima's first observations were of multi-wall nanotubes, he

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observed single-wall carbon nanotubes less than two years later, as did Donald Bethune and colleagues at IBM Almaden in California. In 1996 the Rice group, led by Smalley, synthesized bundles of aligned single-wall carbon nanotubes for the first time. The bundles contained many nanotubes with a narrow distribution of diameters, making it possible to perform experiments relevant to one-dimensional quantum physics. Several groups have now measured some of these remarkable properties, which seem to confirm many of the theoretical predictions.

Focus on structure

A few key studies have explored the structure of carbon nanotubes using high-resolution microscopy techniques. These experiments have confirmed that nanotubes are cylindrical structures based on the hexagonal lattice of carbon atoms that forms crystalline graphite. Three types of nanotubes are possible, called armchair, zigzag and chiral nanotubes, depending on how the two-dimensional graphene sheet is "rolled up".

The different types are most easily explained in terms of the unit cell of a carbon nanotube - in other words, the smallest group of atoms that defines its structure (see top)

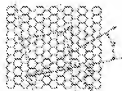
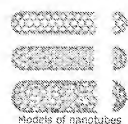


figure a

). The so-called chiral vector of the nanotube, C_n , is defined by $C_n = n\hat{a}_1 + m\hat{a}_2$, where \hat{a}_1 and \hat{a}_2 are unit vectors in the two-dimensional hexagonal lattice, and n and m are integers. Another important parameter is the chiral angle, which is the angle between C_n and \hat{a}_1 .



Models of nanotubes

When the graphene sheet is rolled up to form the cylindrical part of the nanotube, the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotube's circular cross-section, and different values of n and m lead to different nanotube structures (see top)

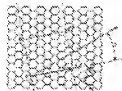


figure a

). Armchair nanotubes are formed when $n = m$ and the chiral angle is 30° (see left figure). Zigzag nanotubes are formed when either n or m are zero and the chiral angle is 0° . All other nanotubes, with chiral angles intermediate between 0° and 30° , are known as chiral nanotubes.

The properties of nanotubes are determined by their diameter and chiral angle, both of which depend on n and m . The diameter, d_t , is simply the length of the chiral vector divided by $\sqrt{3}$, and we find that $d_t = (\sqrt{3}/\pi)a_{c-c}(m^2 + mn + n^2)^{1/2}$, where a_{c-c} is the distance between neighbouring carbon atoms in the flat sheet. In turn, the

chiral angle is given by $\tan^{-1}(\sqrt{3}n/(2m + n))$.

Measurements of the nanotube diameter and the chiral angle have been made with scanning tunnelling microscopy and transmission electron microscopy. However, it remains a major challenge to determine d_t and θ at the same time as measuring a physical property such as resistivity. This is partly because the nanotubes are so small, and partly because the carbon atoms are in constant thermal motion. Also, the nanotubes can be damaged by the electron beam in the microscope.

Since each unit cell of a nanotube contains a number of hexagons, each of which contains two carbon atoms, the unit cell of a nanotube contains many carbon atoms. If the unit cell of a nanotube is N times larger than that of a hexagon, the unit cell of the nanotube in reciprocal space is $1/N$ times smaller than that of a single hexagon.

How to make nanotubes

When the Rice University group found a relatively efficient way to produce bundles of ordered single-wall nanotubes in 1996, it opened new opportunities for quantitative experimental studies on carbon nanotubes. These ordered nanotubes are prepared by the laser vaporization of a carbon target in a furnace at 1200 °C. A cobalt-nickel catalyst helps the growth of the nanotubes, presumably because it prevents the ends from being "capped" during synthesis, and about 70-90% of the carbon target can be converted to single-wall nanotubes. By using two laser pulses 50 ns apart, growth conditions can be maintained over a larger volume and for a longer time. This scheme provides more uniform vaporization and better control of the growth conditions. Flowing argon gas sweeps the nanotubes from the furnace to a water-cooled copper collector just outside of the furnace.

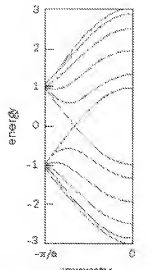
Catherine Journet, Patrick Bernier and colleagues at the University of Montpellier in France later developed a carbon-arc method to grow similar arrays of single-wall nanotubes. In this case, ordered nanotubes were also produced from an ionized carbon plasma, and joule heating from the discharge generated the plasma. Several other groups are now making bundles of single-wall carbon nanotubes using variants of these two methods. However, the Rice group has had the largest impact on the field, largely because it was the first to develop an efficient synthesis method and has formed many international collaborations to measure the properties of single-wall nanotubes.

In a scanning electron microscope, the nanotube material produced by either of these methods looks like a mat of carbon ropes. The ropes are between 10 and 20 nm across and up to 100 μ m long. When examined in a transmission electron microscope, each rope is found to consist of a bundle of single-wall carbon nanotubes aligned along a single direction. X-ray diffraction, which views many ropes at once, also shows that the diameters of the single-wall nanotubes have a narrow distribution with a strong peak.

For the synthesis conditions used by the Rice and Montpellier groups, the diameter distribution peaked at 1.38 ± 0.02 nm, very close to the diameter of an ideal (10, 10) nanotube. X-ray diffraction measurements by John Fischer and co-workers at the University of Pennsylvania showed that bundles of single-wall nanotubes form a two-dimensional triangular lattice. The lattice constant is 1.7 nm and the tubes are separated by 0.315 nm at closest approach, which agrees with prior theoretical modelling by Jean-Christophe Charlier of the University of Louvain-la-Neuve in Belgium and co-workers.

While multi-wall carbon nanotubes do

not need a catalyst for growth, single-wall nanotubes can only be grown with a catalyst. However, the detailed mechanisms responsible for growth are not yet well understood. Experiments show that the width and peak of the diameter distribution depends on the composition of the catalyst, the growth temperature and various other growth conditions. Great efforts are now being made to produce narrower diameter distributions with different mean diameters, and to gain better control of the growth process. From an applications point of view, the emphasis will be on methods that produce high yields of nanotubes at low cost, and some sort of continuous process will probably be needed to grow carbon nanotubes on a commercial scale.



Dispersion relations in nanotubes

Electrons in nanotubes

The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined by the monolayer thickness of the graphene sheet. Around the circumference of the nanotube, periodic boundary conditions come into play. For example, if a zigzag or armchair nanotube has 10 hexagons around its circumference, the 11th hexagonal will coincide with the first. Going around the cylinder once introduces a phase difference of 2π .

Because of this quantum confinement, electrons can only propagate along the nanotube axis, and so their wavevectors point in this direction. The resulting number of one-dimensional conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotube. These simple ideas can be used to calculate the dispersion relations of the one-dimensional bands, which link wavevector to energy, from the well known dispersion relation in a graphene sheet.

Noriaki Hamada and colleagues, then at the NEC Laboratory in Tsukuba, and one of us (RS) have calculated dispersion relations for small-diameter nanotubes (see above right figure). These show that about one-third of small-diameter nanotubes are metallic, while the rest are semiconducting, depending on their diameter and chiral angle (see

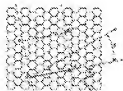
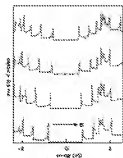


figure a

). In general, an (n, m) carbon nanotube will be metallic when $n - m = 3q$, where q is an integer. All armchair nanotubes are metallic, as are one-third of all possible zigzag nanotubes.

The density of electronic states as a function of energy has been calculated for a variety of nanotubes. As an example, consider the density of states for metallic $(8, 8)$, $(9, 9)$,



figure

(10, 10) and (11, 11) armchair nanotubes (left figure). While conventional metals have a smooth density of states, these nanotubes are characterized by a number of singularities, where each peak corresponds to a single quantum subband. These singularities are important when interpreting experimental results, such as measurements obtained from scanning tunnelling spectroscopy and resonant Raman spectra, the two techniques that have contributed the most to our understanding of the one-dimensional properties of nanotubes.

Although the choice of n and m determines whether the nanotube is metallic or semiconducting, the chemical bonding between the carbon atoms is exactly the same in both cases. This surprising result is due to the very special electronic structure of a two-dimensional graphene sheet, which is a semiconductor with a zero band gap. In this case, the top of the valence band has the same energy as the bottom of the conduction band, and this energy equals the Fermi energy for one special wavevector, the so-called K-point of the two-dimensional Brillouin zone (i.e. the corner point of the hexagonal unit cell in reciprocal space). Theory shows that a nanotube becomes metallic when one of the few allowed wavevectors in the circumferential direction passes through this K-point.

As the nanotube diameter increases, more wavevectors are allowed in the circumferential direction. Since the band gap in semiconducting nanotubes is inversely proportional to the tube diameter, the band gap approaches zero at large diameters, just as for a graphene sheet. At a nanotube diameter of about 3 nm, the band gap becomes comparable to thermal energies at room temperature.

Calculations by one of us (RS) and Charlier show that concentric pairs of metal-semiconductor and semiconductor-metal nanotubes are stable. Nanometre-scale devices could therefore be based on two concentric nanotubes or the junction between nanotubes. For example, a metallic inner tube surrounded by a larger semiconducting (or insulating) nanotube would form a shielded cable at the nanometre scale. One might then envisage nanoscale electronic devices made completely from carbon that would combine the properties of metals and semiconductors, without the need for doping (see *Physics World* 1996 May p18).

Measurements versus theory

Experiments to test these remarkable theoretical predictions have been extremely difficult to carry out, largely because the electronic properties are expected to depend strongly on the diameter and chirality of the nanotube. Apart from the problems associated with making electronic or optical measurements on structures just a nanometre across, it is also important to gain information on the symmetry of the nanotube (i.e. its n and m values). Despite these difficulties, pioneering experimental work has confirmed the main theoretical predictions about the electronic structure of nanotubes.

Early experiments focused on multi-wall nanotubes, since high-quality single-wall nanotubes were not available in great enough quantities. To begin with, however, measurements on individual multi-wall nanotubes did not measure any one-dimensional quantum effects, largely because the diameters of the nanotubes were too large or the studies were not done at low enough temperatures.

Despite these problems, some of the early experiments on individual

multi-wall nanotubes did detect a variety of novel electrical properties, including two-dimensional quantum-interference effects due to weak localization and universal-conductance fluctuations. But the results from multi-wall nanotubes are complicated by simultaneous contributions from concentric nanotubes with different diameters and chiralities. In addition, defects in the nanotubes can lead to electron scattering, and electrical contact cannot be made reliably to all of the constituent nanotubes. The conduction properties of the electrical contacts can also influence electron transport. Further experimental studies of these intriguing transport phenomena should be made on smaller diameter multi-wall nanotubes and at low temperatures, where one-dimensional quantum effects can be observed.

A key breakthrough came in 1994, when Charles Oik and Joseph Heremans of the General Motors Research Laboratory in Michigan measured the properties of individual multi-wall nanotubes using a scanning tunnelling microscope (STM). These results provided the first confirmation that some nanotubes are metallic, while others are semiconducting. Oik and Heremans also showed that the band gap for semiconducting nanotubes is proportional to $1/d$, in agreement with theoretical predictions. However, these techniques are most sensitive to the outer shell of a multi-wall nanotube, since STM probes have a relatively short spatial range. Very recent STM experiments at the Delft University of Technology in the Netherlands have clearly shown the predicted one-dimensional density of states and the difference in behaviour between metallic and semiconducting nanotubes.

Earlier this year, electron transport in an individual single-wall carbon nanotube just a nanometre across was measured for the first time by Cees Dekker and colleagues at Delft, in collaboration with the Rice group. Another group, led by Paul McEuen at the University of California at Berkeley, also working with the Rice group, has also made related measurements on a single rope of single-wall carbon nanotubes (see *Physics World* 1997 June p21).

Both of these studies were carried out at temperatures below 1 K and focused on the "quantum dot" aspect of single-wall carbon nanotubes. Although nanotubes are very much longer than they are wide (typically by a factor of 10^4), the finite length of the tubes still limits the number of allowed wavevectors along the nanotube axis. This gives rise to discrete energy states, which can be determined by measuring the conductance as a function of voltage. For a nanotube 3 μm long, the Delft group found that discrete states near the Fermi level are separated by about 0.6 meV. With the greater availability of single-wall nanotubes, we can expect that voltage-current characteristics will soon be obtained for carbon nanotubes with known n and m values. Such information could then be used to test the one-dimensional dispersion relations predicted by theory.

Since nanotubes are typically a few microns long, electrical contacts can be made by modern lithographic techniques. Single-wall carbon nanotubes thus provide a unique system for studying single-molecule transistor effects, in which an electrode close to the conducting nanotube is used to modulate the conductance.

The energy needed to add an electron to a single-wall nanotube has also been measured. Some 2.6 meV is needed to overcome the Coulomb repulsion between electrons in a nanotube 3 μm long and about 1 nm in diameter. Researchers are now beginning to study these "Coulomb-blockade" phenomena systematically in carbon nanotubes.

Recent progress in synthesizing carbon nanotubes should also

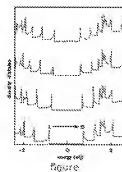
stimulate experimental studies of the junction between metallic and semiconducting nanotubes, which should in turn encourage further discussions about possible electronic applications. Experimental studies on single-wall nanotubes would also test the recent predictions of one of us (RS), and of Hiroshi Ajiki and Tsuneya Ando at the University of Tokyo, about what should happen to the dispersion relations in a magnetic field.

Nanotubes in the light

Some of the most interesting one-dimensional quantum effects of carbon nanotubes have been observed in Raman spectra, which probe the lattice vibrations, or "phonons", in a material through the inelastic scattering of light. One-dimensional dispersion relations for the phonons in nanotubes have been calculated, first by Rudi Jishi of the California State University at Los Angeles using the zone-folding method, and later by Ernst Richter and co-workers at the University of Kentucky using an *ab initio* modelling technique. These calculations show that there are many different vibrational modes, which result from the large number of carbon atoms in the unit cell of the nanotube. In general, more phonon modes appear as the nanotube diameter and the size of the unit cell increases.

Of these vibrational modes, only a few can be excited by Raman scattering. The number of these Raman-active modes is independent of the nanotube diameter, which makes it possible to investigate how the frequency and oscillator strength of each mode depends on the nanotube diameter. Some modes have been found to be highly sensitive to the nanotube diameter, while others are not.

One of us (PE) and colleagues at the University of Kentucky have performed Raman-scattering experiments on ropes of single-wall carbon nanotubes grown by the Rice group, which contain a large concentration of (9, 9) and (10, 10) armchair nanotubes. These experiments exploited the resonant Raman enhancement effect, in which the frequency of the laser light matches the energy of an allowed optical transition between peaks in the density of states (see above left).



). Such a resonance greatly increases the intensity of the observed Raman effect.

The Kentucky group and Bruce Chase at the Dupont Research Facility in Wilmington, Delaware, measured Raman spectra at several different laser excitation energies (figure 5). Since the energies of the electron states depend on the nanotube diameter, a change in laser frequency brings a carbon nanotube with a different diameter into resonance. Prominent in the spectra are a number of modes near a frequency of

1580 cm^{-1} , which show only a weak dependence on nanotube diameter. There is also a strong mode at about 1366 cm^{-1} that is highly sensitive to the nanotube diameter. This feature corresponds to a radial-breathing mode, in which all of the atoms in the nanotube are displaced outwards (or inwards) by an equal amount, so that the symmetry of the network of carbon atoms remains the same throughout the vibration. From the measured frequency of the radial-breathing mode, we can determine the diameter of the nanotube that is in resonance with the laser frequency.



Light scattering from nanotubes

Detecting these quantum effects in the Raman spectra lends strong credence to the idea that single-wall carbon nanotubes have a one-dimensional electronic and phonon structure. These experiments, together with very recent STM observations by Jeroen Wildoer and co-workers at Delft have provided the clearest confirmation to date that the electronic density of states have singularities typical of a one-dimensional system.

Strength in applications

Another exciting area of research is focused on the mechanical properties of carbon nanotubes. By analogy to graphite and carbon fibres, nanotubes are expected to be very strong and have high elastic moduli. In 1996 a group led by Thomas Ebbeson at the NEC Research Institute in Princeton, New Jersey, estimated the Young's modulus of a carbon nanotube by measuring the vibrations of the free end of a nanotube that was clamped at the other end. Their estimates were consistent with the exceptionally high values of Young's modulus already measured for a graphene sheet, about 1 TPa.



figure

Single-wall carbon nanotubes are also expected to be very strong and to resist fracture under extension, just as the carbon fibres commonly used in aerospace applications. According to calculations by Jerzy Bernholc and colleagues at North Carolina State University in Raleigh, a nanotube could be elongated by several per cent before it

would fracture. Unlike carbon fibres, however, single-wall nanotubes are remarkably flexible. They can be twisted, flattened and bent into small circles or around sharp bends without breaking, and severe distortions to the cross-section of nanotubes do not cause them to break (above left)



figure

). Moreover, molecular dynamics simulations by Bernholc and colleagues indicate that in many cases the nanotube should regain its original shape when the stresses distorting it are removed.

Another advantage of nanotubes is their behaviour under compression. Unlike carbon fibres, which fracture easily under

compression, carbon nanotubes form kink-like ridges that can relax elastically when the stress is released. As a result, nanotubes not only have the desirable properties of carbon fibres, but are also much more flexible and can be compressed without fracture. Such excellent mechanical properties could lead to applications in their own right, or in conjunction with other desirable properties.

Richard Superfine and colleagues at the University of North Carolina in Chapel Hill have shown that the mechanical properties of carbon nanotubes would make them ideal for manipulating other nanoscale structures. Advances in understanding carbon nanotubes should therefore have a major impact on the whole field of nanotechnology. Many of the applications now being considered involve multi-wall nanotubes, partly because they have been available for much longer, and partly because many of these applications do not explicitly depend on the one-dimensional quantum effects found mainly in single-wall nanotubes.

It has also been suggested that carbon nanotubes could be used in displays or for the tips of electron probes. Pulickel Ajayan and co-workers at Rensselaer Polytechnic Institute in Troy, New York, have shown that the caps of nanotubes are more chemically reactive than the cylindrical sections, and a group at the Ecole Polytechnique Fédérale Lausanne in Switzerland, then led by Walter ter Heer, has shown that the caps are efficient electron emitters. Other applications could result from the fact that carbon nanotubes can retain relatively high gas pressures within their hollow cores. Charles Lieber of Harvard University has also suggested that carbon nanotubes could act as a template for synthesizing new carbides structured on the nanoscale.

As we have seen, structures based on carbon nanotubes offer exciting possibilities for nanometre-scale electronic applications. In the same way that carbon fibres are used in composites to strengthen a structure or to enhance the electrical conductivity of the main constituent, carbon nanotubes could be combined with a host polymer (or metal) to tailor their physical properties to specific applications. Since carbon nanotubes are so small, they could be used in polymer composites that could be formed into specific shapes, or in a low-viscosity composite that could be sprayed onto a surface as a conducting paint or coating. Fundamental studies of the rheological properties of nanotube-polymer composites will be interesting from both a scientific and a practical point of view.

Intense research into carbon nanotubes is sure to continue for at least the next few years. Quantum effects and other unique features in their electronic structure will be explored further, particularly as well characterized single-wall nanotubes become more widely available. Experiments with single-wall nanotubes will also probe their lattice vibrations, as measured by Raman spectroscopy, and their mechanical properties. As we learn more about nanotubes, producing novel electronic devices and composite materials could just be the start of a variety of future applications.

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